The Parent of Actinium.

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It has been recognised for more than a decade that actinium cannot be a primary radio-element, but hitherto all attempts to obtain evidence of its continuous production, in the same way as has been established for polonium and for radium, have met with no success. As our knowledge of radioactive change has become precise, the conceivable modes in which actinium could originate have been narrowed down and, one by one, experimentally eliminated without the parent of actinium having been discovered. In the present paper an account is given of experiments which have been successful in separating from uranium minerals preparations initially free from actinium but producing that element in the course of years. In 1913, a minute production of actinium, almost too small to be confident of, was recorded by one of us in the old preparations of uranium-X separated from 50 kgrm. of uranyl nitrate in 1909.* The subsequent history of these preparations has confirmed this minute growth, and placed it beyond all doubt, although even now, after eight years, it is still very small in comparison with the growth in the later preparations separated from uranium minerals.

Before dealing with the newer experiments, the opportunity will be taken of giving a fairly full account of the long and involved history of the problem, and of correlating and bringing up to date the evidence that can be derived from these old uranium-X preparations. The experiments were undertaken when the course of the disintegration of uranium and its connection with radium was quite obscure, but the experiments afford valuable data, which has never been properly discussed in the light of recent discoveries, on the possible modes of origin of actinium. With regard to the new work, in the absence of one of us on military service since 1915, the experiments were continued for a time by Miss Ada Hitchens, B.Sc., Carnegie Research Scholar, until she also left to engage in war duties. Her valuable assistance has contributed very materially to the definiteness of the conclusions that it has been possible to arrive at.

History of the Problem.

Although discovered in 1899, by Debierne, actinium still remains probably the least known of all the radio-elements. The statement does not apply to

* F. Soddy, 'Chem. News,' vol. 107, p. 97 (1913).

its numerous family of disintegration products, which are quite as well known as those of radium and of thorium, and the existence of which established beyond all doubt the claim of actinium to be considered a new radio-element. The earlier attempts at the chemical and radioactive characterisation of actinium are of little present significance, for the doubt remains as to how far they refer to actinium itself rather than to its products, radioactinium and actinium-X, or even to ionium, with which the earlier preparations were undoubtedly admixed. Nothing can be said definitely about its period, except that it must be at least of the order of a decade, but may be almost indefinitely longer. The observations by Mme. Curie as to a marked decay occurring in the β-radiation of an old preparation of actinium, to the extent of some 10 per cent. in three years, have not unfortunately been completed or confirmed. They indicated a period of only some 30 years for this element, which it is difficult to accept, as in this case one would have expected evidence of the production of actinium to have been obtained fairly easily.

The researches of Boltwood[*] on the relative proportions of the total α-activity of uranium minerals were the first to throw light on the genetic relations of actinium. The proportionality between the quantities of uranium and actinium which he found, and which has been confirmed by others, indicated that uranium must be the ultimate parent of actinium as well as of radium. But of the total α-activity of the mineral only some 6 per cent. was contributed by the whole actinium series, whereas the radium series contributes some 65 per cent., and the uranium and ionium the remaining 29 per cent. It was pointed out by Rutherford in 1906[†] that on this account actinium could not be an intermediate member of the uranium-radium-polonium disintegration series, for in this case the proportion of the α-radiation contributed by its products would be somewhat greater than that contributed by the radium series. He concluded that it was not a lineal descendant of uranium in the same sense as radium is, but was derived from uranium in much less amount than the products of the radium series. To account for the simultaneous production of two products in different proportions he suggested that, in the rearrangement of the parts of the atom after the expulsion of the α-particle, more than one fairly stable arrangement may be possible, so that two or more products would result, which, though of equal atomic mass, would exhibit differences in chemical properties and be capable of separating from one another, but which would not necessarily be formed in equal amounts.

[*] B. Boltwood, 'Amer. J. Sci.,' IV, vol. 25, p. 269 (1908).
[†] 'Radioactive Transformations,' 1906, pp. 170 and 176.

A slightly different explanation was offered somewhat later,* which ascribed the formation of the branch actinium series to the simultaneous existence of two types of instability in the same atom at the same time, resulting in two modes of disintegration proceeding simultaneously as if each alone were in progress according to the law of simple disintegration. The ratio between the quantities of the two products resulting is, then, that between the periods of the two separate simultaneous changes, whereas the radiation resulting from both modes of disintegration decays exponentially according to the same period, which is the sum of the two separate periods. Definite cases of the branching of a disintegration series were established later by the work of Fajans, and of Marsden and Darwin, for the cases of the C-members of the radium and the thorium series, and it has been proved that the C-member disintegrates dually in two ways. In the one mode an α-particle is expelled, followed by a β-particle in the next change, while in the other mode the order is reversed. All attempts to separate the C-member into two different substances responsible for the two modes of change have failed and both the α- and β-rays expelled in the dual disintegration decay with the same period. Hence, it is not sufficient to suppose that the C-member is a mixture of isotopes, but also that each must have the same period. This is tantamount in its experimental consequences to regarding the C-member as homogeneous, disintegrating dually according to the theory of multiple disintegration.

The simple generalisation that in an α-ray change the element shifts its position in the Periodic Table by two places in the direction of diminishing mass, and in a β-ray change by one place in the opposite direction, put the problem of the origin of actinium in a very definite form. In the first place, it showed that if two products were simultaneously produced in an α-ray change, they would be isotopic and chemically inseparable, so that they would only be distinguishable by a difference of period. On the other hand, the scheme of disintegration adopted for the C-members, in agreement with the theory of multiple disintegration, was, so far as it could be tested, in conformity with the generalisation. Fleck showed that the C-members are isotopic with bismuth, whereas thorium-D formed from thorium-C in the α-mode is isotopic with thallium; but radium-D, formed from radium-C in the β-mode, followed by a subsequent α-change, is isotopic with lead. This confirmation made it possible to apply the theory of multiple disintegration to the problem of the origin of actinium with considerable confidence.

With regard to actinium itself, it had long been expected that it would occupy the hitherto vacant place in the Periodic Table between radium and

* F. Soddy, 'Phil. Mag.' [6], vol. 18, p. 739 (1909).

thorium, on account of its resemblance in chemical character to the rare-earth family of elements, and in particular, as Giesel showed, to lanthanum. Fleck proved this by showing that mesothorium-II is isotopic with actinium. As mesothorium-II is formed in a β-ray change from mesothorium-I, an isotope of radium, it, and also actinium, must occupy the place indicated.[*]

Being in Group III of the Periodic Table, the parent of actinium must be either an isotope of radium, if it is formed in a β-ray change, or, if formed in an α-ray change, its parent must occupy the vacant place in Group V between thorium and uranium. The nearest analogue of this missing element is tantalum, and hence the parent of actinium in this case must be a long-lived, α-ray-giving, " eka-tantalum," still undiscovered. The generalisation further showed that the place in question cannot be vacant, but must be occupied by the then unknown product of uranium-X, which is an isotope of thorium giving β-rays. The first suggestion made is shown below. It was supposed that this unknown product in the VA family, like the C-members in the VB family, disintegrated dually, the main product being uranium-II in a β-ray change, and the branch product being actinium in an α-ray change.[†]
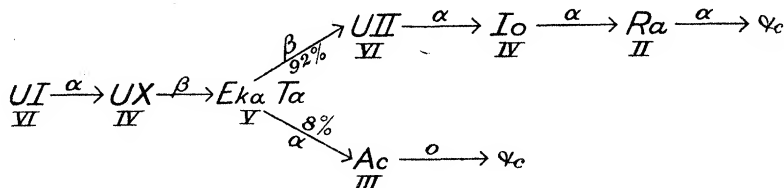
The discovery soon after, by Fajans and Göhring,[‡] that uranium-X consisted of two successive products, uranium-X_1 and uranium-X_2, both giving β-rays, and that uranium-X_2 was a very short-lived element, with period 1·65 minutes, responsible for the more penetrating β-rays of uranium-X, disproved this view. Being the first occupant of the vacant place between uranium and thorium to be discovered, uranium-X_2 was given the distinctive name " Brevium."

The alternative suggestion that actinium was the product of radium, or an isotope of radium, in a β-ray change was then definitely disproved by the examination of a specimen of radium bromide, containing 13·2 mgrm. of radium element, prepared by Giesel 10 years before, and untouched chemically since preparation. Not the least trace of radioactinium could be detected in this preparation, though the isotopic radiothorium, present in minute amount because of the existence in Joachimsthal pitchblende of an
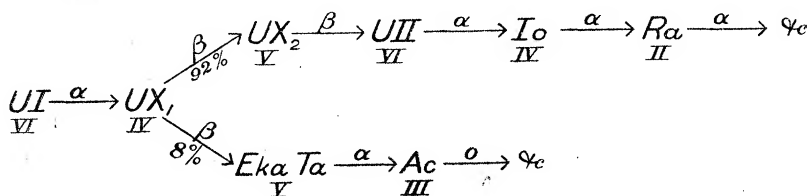
[*] A. Fleck, ' Trans. Chem. Soc.,' vol. 103, pp. 388 and 1052 (1913).

[†] F. Soddy, 'Chem. News,' vol. 107, p. 97 (1913).

[‡] Fajans and Göhring, ' Physikal. Zeitsch.,' vol. 14, p. 877 (1913).

infinitesimal amount of thorium, was clearly detected.[*]   This has been confirmed by Paneth and Fajans with a preparation containing 180 mgrm. of radium, six years old.[†]

The remaining possibility that eka-tantalum was the direct parent of actinium was revived in a new form by Hahn and Meitner.[‡]   Hitherto, it had been supposed that, as in the case of the C-members, the radiations accompanying the dual modes were different, being α-rays in the one case and β-rays in the other.   Hahn and Meitner suggested that the change of uranium-X_1 might be dual, both modes giving β-rays, so that there would be two isotopes of eka-tantalum produced, one the known uranium-X_2, or brevium, the other giving actinium in an α-ray change.   This suggestion is shown below.

$$UI \xrightarrow{\ \alpha\ } UX_1 \left\{ \begin{array}{l} \xrightarrow[92\%]{\ \beta\ } UX_2 \xrightarrow{\ \beta\ } UII \xrightarrow{\ \alpha\ } Io \xrightarrow{\ \alpha\ } Ra \xrightarrow{\ \alpha\ } \&c \\ \xrightarrow[8\%]{\ \beta\ } Eka\,Ta \xrightarrow{\ \alpha\ } Ac \xrightarrow{\ o\ } \&c \end{array} \right.$$

This scheme still has to be regarded as a possible, if not the most probable, mode of origin of actinium, always provided that the isotope of eka-tantalum producing it has a very extended period of life.   For, if true, there must be a growth of α-radiation accompanying the decay of the β-radiation of the uranium-X.   A laborious investigation on this very point was carried out by one of us in 1909.[§]   No such growth could be detected in the several preparations of uranium-X separated from 50 kgrm. of uranyl nitrate, so that, if it occurred, it must be minute.   The preparations always possessed an appreciable α-activity, which remained constant, while the β-rays decayed, and subsequently during the eight years since · preparation. Making allowance for the fact that only 8 per cent. of the atoms of uranium-X_1 produce this supposed parent of actinium, a re-examination of the data of these old experiments leads to the definite conclusion that, for Hahn and Meitner's scheme to be in accordance with them, the period of average life of the supposed parent of actinium cannot be less than 10,000 years.   The growth of α-radiation, during the decay of the β-rays, would certainly have been detectable if the period had been less than this as a minimum.

* F. Soddy, ' Nature,' vol. 91, p. 634 (1913).
† Referred to by C. Göhring, ' Physikal. Zeitschr.,' vol. 15, p. 642 (1914).
‡ Hahn and Meitner, ' Physikal. Zeitschr.,' vol. 14, p. 756 (1913).
§ F. Soddy, ' Phil. Mag.' [6], vol. 18, p. 858 (1909) ; vol. 20, p. 342 (1910).

Thus, if λ_1 is the fraction changing per year of uranium-I, and λ_2 that of the supposed eka-tantalum, and if 0·92 of the atoms follow the radium and 0·08 the actinium mode of disintegration, the quantity of eka-tantalum produced per year is $0·08\,\lambda_1$ times that of the originating uranium. Its α-radiation is $\lambda_2/1·92\,\lambda_1 \times 0·08\,\lambda_1$, or $0·045\,\lambda_2$ times that of the originating uranium. The uranium-X in equilibrium with uranium is 35·5 days' production, and the α-radiation of the eka-tantalum resulting is $35·5/365 \times 0·045\,\lambda_2$, or $0·0044\,\lambda_2$ times that of the originating uranium. But the uranium-X preparation last separated in September, 1909, weighed 78 mgrm., and initially contained the uranium-X in equilibrium with 5·05 kgrm. of uranium. Its α-activity is one-third of that of a similar surface of uranium oxide, and a change of 10 per cent., equal to the α-rays of 2·3 mgrm. of uranium, during the decay of the β-rays, would have been with certainty detected. That is to say, $0·0044\,\lambda_2$ is less than $2·3/5050000$, and therefore $1/\lambda_2$, the period of average life of the supposed eka-tantalum, is certainly greater than 10,000 years.

The subsequent growth of actinium by these preparations will be dealt with later.

The scheme which recommends itself as the most probable mode of origin of actinium, and which has been the starting-point of the present investigation, follows that of Hahn and Meitner in regarding both modes of disintegration to be accompanied by the same type of radiation, but puts the branching-point still one member further back, and the rays emitted as α- instead of β-rays. In 1911 Antonoff * found that certain preparations of uranium-X, separated from uranium by addition of an iron salt and precipitating it by boiling, showed an abnormality in the soft β-radiation emitted, which decayed more rapidly than the penetrating β-rays during the first week from preparation, whereas uranium-X, separated by adsorption with barium sulphate, did not show this peculiarity. The effect he attributed to the existence of a new product of uranium, which he named uranium-Y, with a period of average life of 1·5 days, giving soft β-rays on disintegration, which are somewhat more penetrating than those given by uranium-X$_1$. He suggested that uranium-Y is probably the first member of the actinium series, the ratio between the radiations of uranium-X and uranium-Y being of the expected order for members in the radium and actinium branches respectively. Great difficulty was experienced in repeating these results, but they were subsequently confirmed, as regards the existence of uranium-Y and its probable connection with the actinium series.† It was shown that

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* G. N. Antonoff, 'Phil. Mag.' [6], vol. 22, p. 419 (1911) ; vol. 26, p. 1058 (1913).

† F. Soddy, 'Phil. Mag.' [6], vol. 27, p. 215 (1914).

the chemical method of separating the uranium-X from the uranium is of no significance, but that the essential condition for the decay of uranium-Y to be observed is that the time of reaccumulation of the uranium-X after separation from the uranium must be short. Uranium-Y is isotopic with uranium X_1, and can only be detected by the difference in period. To account for its relation to uranium on the one hand, and uranium-X on the other, the following schemes were suggested.*
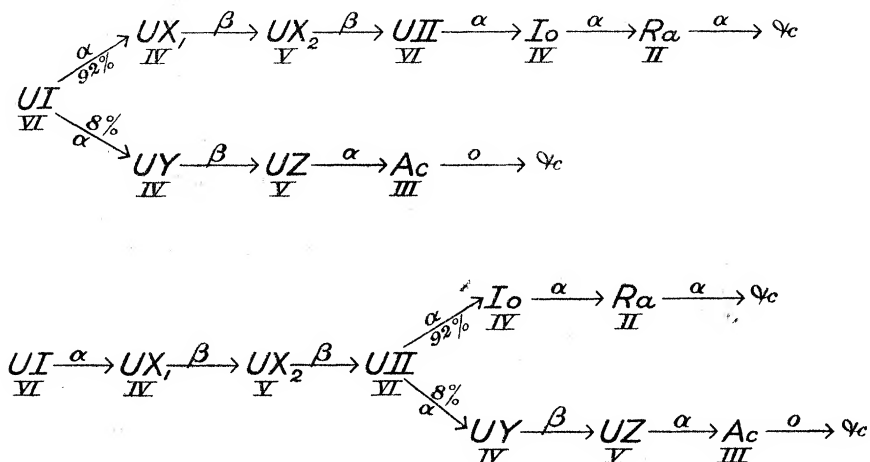

Fig. 1.

The two schemes shown (fig. 1), in which uranium-I in one case and uranium-II in the other are regarded as the parent of uranium-Y, are experimentally indistinguishable at present, and may therefore be regarded as one, but on general grounds the first seems the more probable. The new member, termed uranium-Z in the diagram, to indicate that it is the product of uranium-Y, is the supposed missing direct parent of actinium, occupying the eka-tantalum place in the Periodic Table, isotopic with uranium-X_2 or brevium, and distinguished from it by its long period and by its giving α- instead of β-rays.

According to this scheme no growth of α-rays during the decay of the β-rays of uranium-X is to be expected, for the uranium-Y is so short lived that, in the experiments referred to, hardly any would survive the purification process, after the separation from the uranium, and before the first measurements were made. On the other hand, the constant α-radiation of the preparations, assuming initial α-ray-giving impurities to have been all removed in former separations, would be due to the ionium formed between separations, since ionium is isotopic with uranium-X. The determination

* Compare also 'Chemical Society's Annual Reports,' vol. 10, p. 268 (1913).

of the period of ionium as 100,000 years* enables the α-radiation from this source to be calculated. If λ_3 is the constant of ionium, 10^{-5} (year)$^{-1}$, the α-rays due to the ionium, in comparison with those of the originating uranium, should be $(0.92/1.92)\lambda_3 T$, where T is the time of accumulation in years. This is $5 \times 10^{-6}T$. For the preparation referred to T was 0.25 year, and the found α-activity, that of 22 mgrm. of uranium, was 1.1×10^{-6} of the originating uranium, 20 kgrm. Hence the α-radiation is almost exactly of the magnitude to be expected if it was due to ionium alone.

But this exact agreement must be accidental, for all the ionium formed could not have been separated from the large quantity of uranium. Indeed, since uranium-X_1 is isotopic with ionium, it is possible to calculate fairly closely what proportion was separated, and this proportion amounts to one-third of that present. But the experiment indicates satisfactorily that the α-radiation of this uranium-X preparation from the fourth and last separation carried out, is not much greater than can be accounted for by the ionium alone, which somewhat limits the possibilities to be considered. As soon as the opportunity occurs, it is proposed to repeat these uranium-X separations, when it is to be expected that more definite data as to the periods in the early part of the uranium disintegration series will be thus obtained.

Quite recently, a new suggestion has been made as to the origin of actinium,† namely, that it is derived, through uranium-Y and eka-tantalum, from a third isotope of uranium, to which the name actino-uranium is given, which does not belong to the uranium-radium family, but is a primary radio-element, of atomic weight greater than that of uranium, viz., 240, that of uranium-I being 238. This explains the figure 238·16, found for the atomic weight of uranium, since $0.08 \times 240 + 0.92 \times 238 = 238.16$, and also the integral values of the atomic weight of radium, 226, and of uranium-lead, 206. Assuming that there is constancy of proportionality between the uranium and actino-uranium in minerals, as the constancy of proportionality between uranium and actinium seems to indicate, the suggestion involves the further assumption, not considered by the author, that the periods of uranium-I and actino-uranium must be the same, and a mixture of isotopes in constant proportions, both having the same period, but giving different products, is indistinguishable experimentally from a single substance disintegrating dually. So far as the present problem is concerned, the suggestion may be regarded as a third possibility giving the same consequences as the two shown in fig. 1. At the same time, the atomic weight evidence and, also, as pointed out by the author, the difference in the value of the constants in

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* F. Soddy and Miss A. Hitchins, 'Phil. Mag.' [6], vol. 30, p. 209 (1915).

† A. Piccard, 'Arch. Sci. Phys. Nat.' [4], vol. 44, p. 161 (1917).

the Geiger-Nuttall relation for the radium and actinium family are in favour of this suggestion, that the actinium and radium families may be quite distinct.* It is very desirable that the accepted conclusion as to the constancy between uranium and actinium in minerals should be more rigorously tested.

Growth of Actinium in Old Uranium-X Preparations.

As recorded,† actinium was present in the first uranium-X preparation separated in 1909 from 50 kgrm. of uranyl nitrate in quite obvious and unmistakable quantity, and in the second preparation separated it could be detected, but it was only one-fifteenth as great as in the first, whereas none could be detected in separate tests on each of the three preparations of the third separation or in the single preparation of the fourth separation. A year from preparation, a combined test, on the four latter together, showed a just detectable actinium active deposit. This increased in amount, until at the end of 1912 it was clearly detectable, though very small, and it has since then rather more than doubled in amount, and now (December, 1917) it causes an increase in the leak of the rather insensitive instrument at present used of about 1·5 divisions per minute, the natural leak being 1·0 d.p.m.

This was the first growth of actinium observed, and it is probably to be ascribed to a minute amount of the parent of actinium existing as an impurity in the uranium rather than to a growth of this element, since the preparation was separated from the uranium. The earlier preparations also show a slight increase in the amount of actinium present, but the increase is not much, if any, greater than in the later ones.

The Separation of Eka-tantalum from Pitchblende

Early attempts to separate the supposed parent of actinium from pitchblende, based on its expected analogy in chemical character to tantalum, led to no positive result, probably because only small quantities of pitchblende were available. Solutions of the mineral in nitric acid were shaken with small quantities of tantalic acid, and the latter then kept under observation for the growth of actinium. Similar negative results have been recorded by O. Göhring‡ in the same field. A comparison of the properties of the compounds of niobium and tantalum, and the methods of separating these elements, led to the following process being tried, first on uranium-X,

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* F. Soddy, 'Chemistry of Radio-elements,' Part II, p. 29 (1915).

† F. Soddy, 'Phil. Mag.' [6], vol. 20, p. 344 (1910) ; 'Chem. News,' vol. 107, p. 97 (1913).

‡ O. Göhring, 'Physikal. Zeitsch.,' vol. 15, p. 642 (1914).

to ascertain whether it was capable of separating uranium-X_2, the isotope of eka-tantalum, from uranium-X_1, the isotope of thorium. When this was found to be successful, the method was tried first on small and then on large amounts of pitchblende. The specimen of pitchblende used was from a very fine block of practically pure Indian pitchblende, found to consist of 86 per cent. U_3O_8, 11·9 per cent. PbO, 1·9 per cent. ThO_2, and 0·6 per cent. SiO_2. The figure for the uranium may be too high, and has still to be checked by a radium estimation.

The material was heated in a quartz tube in a current of dried air, charged with the vapours of carbon tetrachloride by passing it through that liquid, kept a few degrees below its boiling-point. It was expected that, under these circumstances, an element resembling tantalum would volatilise at a lower temperature than the other pre-emanation disintegration products in the mineral. In a trial with uranium oxide and tantalic acid, placed side by side in two boats in the tube, it was found that, at a temperature in the neighbourhood of visible red-heat, at which the tantalic acid volatilised freely, the uranium did not volatilise at all. The oxide, in fact, gained weight through absorption of chlorine.

Using a preparation of uranium-X, it was found that, even at a temperature below a visible red-heat, a considerable part of the uranium-X_2 volatilised. The boat containing the uranium-X preparation was removed from the furnace, and measurements of the penetrating β-rays started as rapidly as possible. The quartz boat was chilled externally by water after removal from the furnace. The curves shown in fig. 2 indicate the growth of
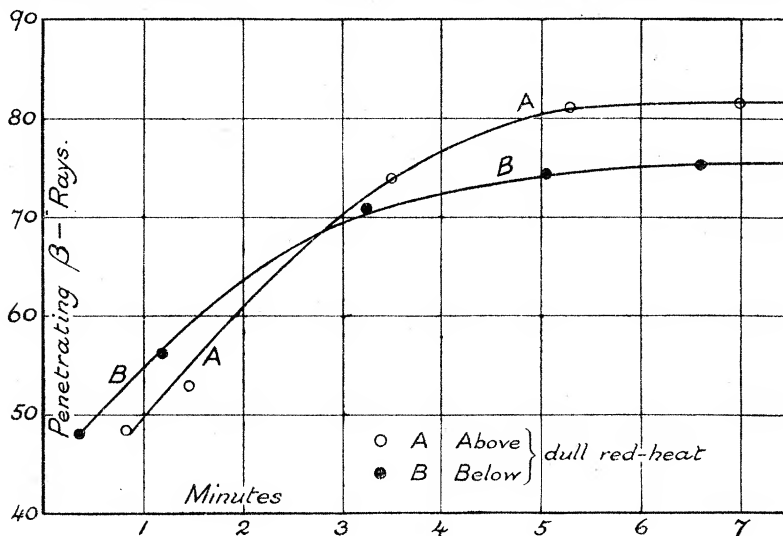

Fig. 2.

the penetrating rays, due to uranium-X_2, after removal from the furnace. For the curve marked A the temperature was just visible red-heat, and for that marked B just below visible red-heat. The results indicate that, even in the very short period of uranium-X_2, a large proportion of it is removed by this treatment. It follows, therefore, *à fortiori*, that the method should be capable of removing the predicted element, since it is isotopic with uranium-X_2, and must have a very extended period of average life.

In the experiments with pitchblende, it was found that only a very small part of the material volatilised at temperatures in the neighbourhood of visible red-heat. The sublimate had a high α- and β-activity, the former being for the most part due to polonium, as shown by its subsequent history, and the latter to radium-E, as shown by its absorption coefficient. But none of the known pre-emanation members could be detected in the sublimate, so that there was nothing present which would interfere with the active deposit test for the presence of actinium.

In the main experiment 470 grm. of finely powdered pitchblende were used. It was heated in the carbon tetrachloride stream just below visible red-heat for 22 hours, the boat containing the material being several times removed during the sublimation, and the contents well mixed before it was replaced. In this operation the material gained 25 grm. in weight through absorption of chlorine, and the sublimate obtained weighed 5 grm. The sublimate was put back in an empty boat, and re-sublimed, as before, for four hours. The second sublimate weighed 0·28 grm. It was washed into a platinum capsule with hydrochloric acid, and dried on the water-bath. It will be termed Preparation I, the date of preparation being March 18, 1915.

The part not sublimed in the two processes described was re-sublimed, as before, at the same temperature, but for a further period of 90 hours. The considerable amount that sublimed was re-sublimed as before, and a second preparation, weighing 2·45 grm., obtained. It was dried on a crucible lid and mounted in a shallow lead tray, a platinum wire being fixed to make contact between the preparation and the lead tray. It is termed Preparation II, the date of preparation being May 10, 1915.

It was thought that Preparation I would contain most, if not all, of the eka-tantalum if present in the mineral, and that Preparation II would give an indication whether the separation in the first operation had been complete or not. After the foregoing treatment, a third preparation was obtained by Miss Hitchins from the same material, by carrying out the sublimation at a much higher temperature, in order to make sure that all the eka-tantalum present was removed. Heating was continued for six or seven hours in all, and the temperature attained was a bright red heat. A considerable quantity

of bright yellow sublimate was so obtained, which, very surprisingly, was found to be free from uranium and to consist mainly of lead chloride. The absence of uranium was surprising, as uranium oxide had been found to sublime at much lower temperature than here employed, and the point is under further investigation.

A small part of the sublimate could not be made to dissolve and was mounted separately on a copper tray. It weighed 0·5 grm., and constitutes Preparation III C. The lead from the solution was precipitated with sulphuric acid and the filtrate precipitated by ammonia in two fractions. Both were dried on copper trays, the first precipitate, III B, weighed 2·4, and the second, III A, weighed 0·4 grm., the date of preparation being December 14, 1915.

Thus from 470 grm. of Indian pitchblende three preparations were obtained by sublimation in carbon tetrachloride vapour, the I and II at below visible red-heat for 22 and 90 hours respectively, and III at a very much higher temperature.

Method of Testing for the Presence of Actinium.

The preparations were kept in a desiccator, and tests for the presence of actinium carried out at intervals. Owing to the exigencies of the time, the intervals elapsing between the tests were rather irregular, and in one case over a year elapsed between successive tests. The preparation was covered with a metal plate, insulated by a rubber or mica washer and connected to the negative pole, the plate being connected with the positive pole of the 220 V. direct current mains. Equilibrium for the actinium active deposit is attained practically in four or five hours, and the exposure was usually over-night. In a few cases of shorter exposure the necessary correction was supplied from the table of the decay of the actinium active deposit given in Makower and Geiger's 'Practical Measurements in Radioactivity,' p. 147. After exposure the plate was removed as quickly as possible to a simple α-ray electroscope, and readings commenced as soon as possible after the disturbance caused by the opening of the electroscope had subsided and continued for four and five hours. The decay curve over this period was plotted and the constant determined from the curve. If the activity is due to actinium the activity decays exponentially,—after an initial some-what slower rate of decay extending over the first few minutes caused by actinium-C of period 3·1 minutes,—with the period of actinium-B, 51 minutes. The character of curve shows at once whether it is due to actinium, for although the period of radium-B, 38·5 minutes, is not very greatly different from that of actinium-B, the active deposit could not possibly

be mistaken for that of radium, since the latter would show the large rapid initial decay due to radium-A.

Observations on the Growth of Actinium.

Preparations I and II, when prepared, gave completely negative results when tested as described during the period covered by the first few weeks from preparation. Not the slightest detectable growth of actinium has yet occurred in Preparation I, in which it was thought that the main quantity of eka-tantalum would be concentrated, though over 2·5 years have elapsed since preparation. Neither has there been any growth in Preparation III, a minute initial activity in III C having, if anything, decreased. But in Preparation II there has been a continuous growth of actinium, so that now, after 2·6 years from preparation, the leak in the electroscope due to the active deposit of actinium amounts, initially to over 10 divisions per minute. This is 20 times as much as could be with certainty detected, and 10 times as much as could be with certainty characterised as due to actinium.
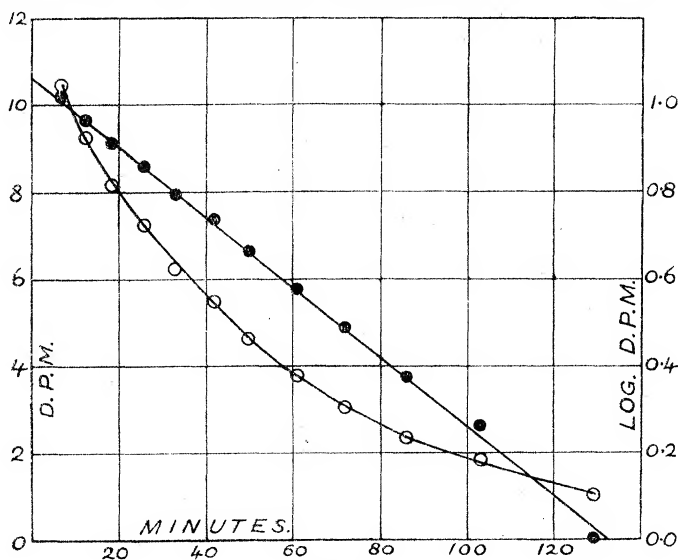

Fig. 3.

The decay curve of a recent measurement of this preparation, 2·6 years from preparation, is shown in fig. 3. The value of the period as calculated from the slope of the logarithmic decay curve is 53·5 minutes, that of actinium-B being 52·1 minutes, and the curve is that to be expected of a pure actinium active deposit.

Fig. 4 shows the growth of actinium with time for this preparation. It indicates the expected initial period of retardation due to the members radio-

actinium of period 28 days, and actinium-X of period 16·4 days, and after that a regular increase with time. The quantitative estimation of actinium
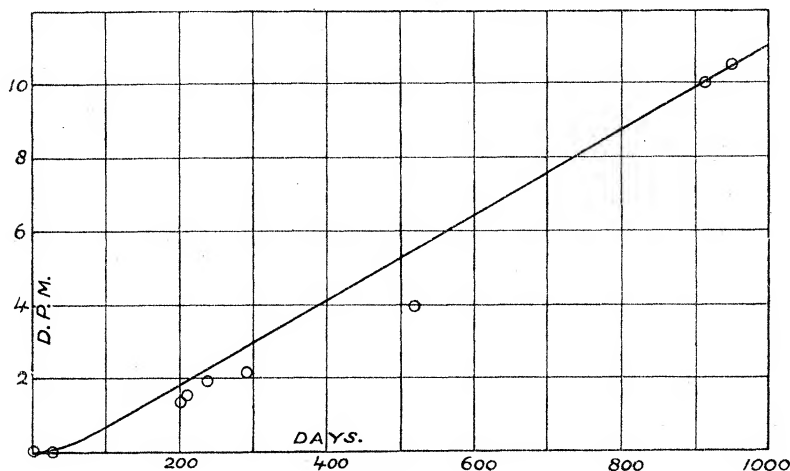

Fig. 4.

is of course very much more uncertain and difficult than that of radium, and, indeed, there has been little or no work practically attempted yet in this field, and it may be doubted whether a really accurate method applicable to very minute quantities is yet possible. No great consistency is to be expected from the method described, for the solid preparation probably varies somewhat in emanating power. The moisture of the atmosphere on the day of testing is, as will be shown later, an important factor. For this reason it would be premature to build much upon the precise form of the curve, and the indication that it gives of an increase in the rate of growth of actinium with the lapse of time, and an increase of slope in the later measurements. Not enough measurements have been taken, and the method is too uncertain to justify the conclusion that this indicates the existence of intermediate bodies between the eka-tantalum and the actinium. For we know, from the α- and β-ray change rules, that three, if any, such intermediate bodies must intervene, and this is not very probable.

Thus, contrary to expectation, instead of the main part of the parent of actinium being in the first sublimate obtained, it is, so far as can be seen, contained wholly in the second, and neither the first nor third preparations contain a detectable amount. The second preparation was obtained by merely continuing the process of sublimation at the same temperature as the first for a further 90 hours after an initial 22 hours, so that it is surprising that the whole of the eka-tantalum should appear to be in the second preparation. The probable explanation is that the eka-tantalum does not

commence to volatilise until the material has become saturated to a certain point with chlorine. In the case of the large mass of material used, this preliminary to the process would of necessity take a considerable time.

A Separation of Eka-tantalum from Joachimsthal Pitchblende.

A similar growth of actinium to that in Preparation II has occurred in another preparation obtained differently. In 1903, a kilogramme of very fine selected Joachimsthal pitchblende, probably containing over 60 per cent. of uranium, was dissolved in nitric acid, and the solution filtered. The clear solution gradually deposited a small white precipitate, and subsequent examination showed that almost all the radium had precipitated from the solution. This spoiled the material for the purpose for which it had been prepared, and the solution and precipitate were left together in the bottle till 1908. Probably sulphides in the mineral had been oxidised to sulphate by the nitric acid, accounting for the precipitation of the radium. In May, 1908, the precipitate was filtered off, the filtrate evaporated to dryness, redissolved in water and again filtered, and the total insoluble material, after thorough digestion with strong nitric acid, was washed, dried, and preserved. It weighed 8 grm., and its α-activity was recorded as about five times as great as that of uranium oxide. In May, 1914, about one-quarter of the material was subjected to the carbon tetrachloride sublimation, under similar conditions to those described for Preparations I and II. It was thought that any element in the pitchblende resembling tantalum in chemical properties would most probably be contained in this precipitate, and this view was supported by the fact that in 1914 it contained an easily detectable quantity of actinium, which one would hardly have expected to have been present initially, but which had probably grown since preparation.

The preparation obtained by sublimation gave an actinium active deposit initially (May, 1914) of 2 to 2·5 divisions per minute, which had increased in August, 1914, to rather more than 3 d.p.m. At present (November, 1917) it gives an active deposit of about 12 d.p.m., slightly greater than that given by Preparation II. In age it is about 100 days older. Some of the original material was spread as a film on a copper tray, and its α-activity compared with that of a similar film of uranium oxide. In May, 1914, the activity was about three times as great as the uranium, but, recently tested, the activity was found to have increased to about 5·6 times. This is probably of not much present significance, as such an increase is to be expected if radium D is present, as it is almost certain to be.

The results with this preparation are thus confirmatory to those described, but the history of the material is more involved and the exact amount of

mineral from which it was derived less definite than in the former case. There are certain lacunæ to be filled up, and this cannot be done till after the war.

Theory of the Growth of Actinium from Eka-tantalum.

If the scheme assumed (fig. 1) is correct, and actinium is the direct product of eka-tantalum, it follows that the growth of actinium should proceed linearly with the time, if both substances are of long life in comparison with the time of observation. In this scheme let A, B, C, D be the quantities respectively of eka-tantalum, actinium, radioactinium and actinium-X, their radioactive constants being, λ_1, λ_2, λ_3, λ_4. The amount of active deposit obtained should vary as D if the emanating power of the preparation remains constant.

The growth of actinium being given by

$$d\mathrm{B}/dt = \lambda_1\mathrm{A} - \lambda_2\mathrm{B},$$

it follows, if both actinium and its parent are long-lived, that the first term may be regarded as a constant and the second term neglected in comparison with it. Hence, if t is the time

$$\mathrm{B} = \lambda_1\mathrm{A}t.$$

The growth of radioactinium, initially absent, is given by

$$d\mathrm{C}/dt = \lambda_2\mathrm{B} - \lambda_3\mathrm{C},$$

so that

$$\mathrm{C} = (\lambda_1\lambda_2/\lambda_3)\,\mathrm{A}\,\{t - 1/\lambda_3 - (1/\lambda_3)\,\epsilon^{-\lambda_3 t}\}.$$

Similarly, the quantity of actinium-X is given by

$$\mathrm{D} = (\lambda_1\lambda_2/\lambda_4)\,\mathrm{A}\,[t - 1/\lambda_4 - 1/\lambda_3 + \{\lambda_4/\lambda_3\,(\lambda_4 - \lambda_3)\}\,\epsilon^{-\lambda_3 t}$$
$$- \{\lambda_3/\lambda_4\,(\lambda_4 - \lambda_3)\}\,\epsilon^{-\lambda_4 t}].\quad (1)$$

The last two terms within the bracket become zero as t increases, and may be neglected after the first six months, when what Rutherford terms "transient" equilibrium, of the active deposit products with the actinium, is attained. After that initial period the growth of active deposit is given by a straight line cutting the zero axis at a time $1/\lambda_3 + 1/\lambda_4$, or 44·5 days, from the start. The curve in fig. 4 represents a theoretical curve according to expression (1) above, and the departure from this curve is not sufficiently great to justify yet any conclusion that the production of actinium from eka-tantalum is not direct.

If eka-tantalum is the direct parent of actinium and both are long-lived, the growth of actinium is in every respect analogous to the growth of radium from ionium, studied by Boltwood. Just as Rutherford and Boltwood were able to deduce from the rate of growth of radium the period of radium, knowing nothing about the period of ionium except that it was very long, so it should be possible to find the period of actinium from its rate of growth

without knowing anything as to the period of eka-tantalum; this can be done if Preparation II contains the whole of the eka-tantalum originally in the mineral, and as none can be detected in the other preparations from it, this may be provisionally assumed. Then the $\lambda_1 A$ of the above equations is equal to and may be replaced by $\lambda_4 D_0$, where D_0 is the equilibrium quantity of actinium-X in 470 grm. of the original mineral. After transient equilibrium is reached

$$D/D_0 = \lambda_2 (t - 1/\lambda_4 - 1/\lambda_3)$$

or $$1/\lambda_2 = D_0/D (t - 44\cdot5 \text{ days}).$$ (2)

The period of actinium is thus given by the ratio between the actinium-X present in the 470 grm. of mineral, and that in the preparation separated from it, multiplied by the age of the preparation less 45 days.

Provisional Determination of the Period of Actinium.

What is therefore needed is to compare the actinium active deposit, now given by Preparation II, with that given by a known weight of the Indian pitchblende under the same conditions. The proportion of the emanation generated in the preparation contributing to the measurements of the active deposit in fig. 3 was quite unknown, and, owing to the very short period, cannot even be guessed. The problem to be solved is a difficult one, and although, in the following attempt, the estimate of the period arrived at is considered a probable one on the specified theoretical assumptions made, it must not be regarded as entirely free from the possibility of serious experimental error. But it seemed to be worth while making the attempt at the present stage, even at the risk which, unfortunately, has actually been incurred, of interrupting irrevocably the sequence of observations on the growth of actinium in this preparation, and possibly losing some of the eka-tantalum it contains.

The preparation was found, on chemical examination, to be, as was to be expected, a very heterogeneous material. It appeared to consist principally of lead and uranium chloride, and could not be got completely into solution in the small volume of water that had to be used for the test. In the first direct comparison with pitchblende, the material was transferred to a weighing bottle, in the stopper of which tubes for leading through a current of gas were fused. The volume of the bottle was 17 c.c. A little pure nitric acid was added, and most of it evaporated off, then water, making a final volume of 8 c.c. Solution was only partial, and lead chloride crystallised out on cooling. In the test there was a considerable amount of solid with the solution. For the comparison standard, 1 grm. of the original pitchblende in nitric acid solution was made up to the same volume in a precisely similar weighing bottle.

The apparatus used for the comparison is shown in fig. 5. It was designed to secure as large a proportion of the active deposit of actinium,
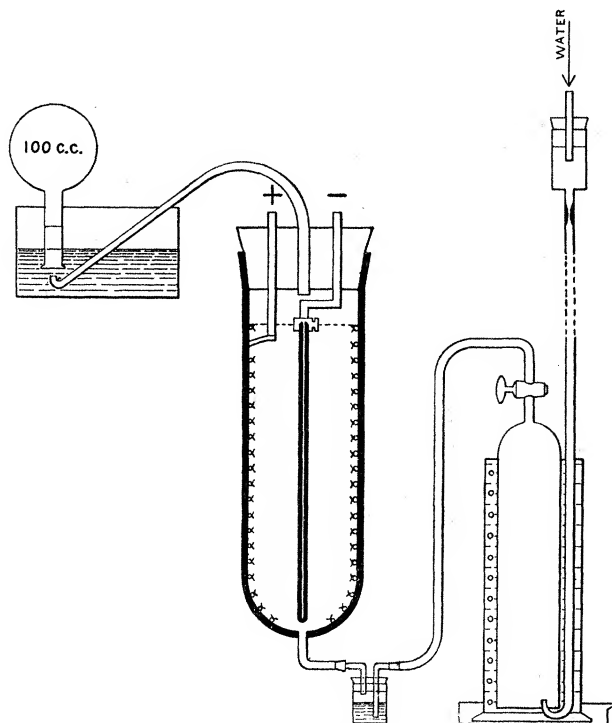

FIG. 5.

whilst suppressing that due to radium and thorium in the mineral. A constant stream of air, of 430 c.c. a minute, was sent through the solution, from a water-dropper delivering air into a reservoir under constant pressure, secured by causing an excess of air always to escape through the water at the bottom of the reservoir. The air stream was led into a glass cylinder of 250 c.c. volume, lined with wire gauze, connected with the positive main, and along the axis of the cylinder was hung a strip of aluminium foil connected with the negative main. The strip was doubled, and the two halves pressed together in close contact and clamped by a binding screw attached to the cork. The air stream was continued for an hour, the aluminium strip opened out, cut in pieces, and introduced into the electroscope active side uppermost, measurements being taken as usual.

Under these circumstances, the actinium active deposit obtained from Preparation II was only one-quarter of that obtained from the same preparation in the solid state, and it was equal to that given by 0·25 grm. of the original pitchblende in solution. In the case of the latter, the effect

due to the thorium present could be detected, but it was small in the case of an hour's run, and could be very readily corrected for. The actinium active deposit given by the pitchblende solution was only from one-sixth to one-fourth of that which it was calculated it should have given, if all the actinium emanation generated had been effective. A delay of only 8–10 seconds between the time of formation of the emanation by the disintegration of actinium-X and its arrival in the testing vessel would account for this difference. The delay in the passage through the dead space above the liquid in the weighing bottle was only 1·7 seconds, so that it appears that, in solution, the greater part of the actinium emanation disintegrates before it can be swept out of the liquid phase. This is very unfortunate, as it means that, for accurate measurements by the solution method, some four to six times the quantity of raw material must be worked up, or four to six times the period waited for the effects than would theoretically be necessary. The fact that Preparation II gave some four times as much active deposit in the solid state as in solution indicates that the emanating power of the solid preparation was surprisingly high, and not much short of the maximum possible. This conclusion is consistent with all the subsequent results obtained with it.

Further attempts were then made to get the whole of Preparation II in solution. The chlorine was first removed, by dissolving as much as possible in boiling water, adding ammonium carbonate to convert the lead into carbonate, filtering and washing the precipitate, and re-dissolving it in nitric acid. The filtrate, which deposited ammonium uranate on evaporation, was cautiously ignited, to expel ammonium chloride, and the residue re-dissolved in the nitric acid solution of the precipitate. A small insoluble residue, weighing rather less than 0·1 grm., was filtered off, and the filtrate got back in the weighing bottle as a clear solution. Comparison of this with a new 0·25 grm. pitchblende standard nearly confirmed the previous result with the partial solution, and showed the amount of actinium-X to be that in 0·20 grm. of pitchblende.

The small insoluble residue was treated with hydrofluoric acid, when very nearly all went into solution without effervescence, leaving a jelly on evaporation. To remove hydrofluoric acid, the material was treated with ammonia, evaporated, and, thoughtlessly, ignited to expel ammonium fluoride, overlooking the possibility that this procedure might cause some of an element resembling tantalum in properties to volatilise. The ignited residue weighed only 0·0175 grm. The loss may have been entirely silica, but it is feared some of the eka-tantalum may also have been volatilised. The minute residue, however, was extremely active, giving an α-radiation corresponding

with that of some 60 cm.² surface of uranium oxide. But in this state an active deposit test failed to show the presence of actinium. So far as can be guessed from its expected chemical analogy with tantalum, this small insoluble residue is likely to contain the eka-tantalum, but only its future history can disclose this.

It thus appears from the foregoing comparison that the amount of actinium-X grown in Preparation II from 470 grm. of pitchblende, in 2·55 years + 45 days is equal to the amount of actinium-X in about 0·25 grm. of the original material. The period of average life of actinium is thus about 5000 years on the assumptions made, viz.: (1) that actinium is the direct product of the element producing it in the preparation; (2) that the preparation contained all of this direct parent that was present in the mineral; (3) that the comparison with pitchblende did not involve any serious error, owing to the chemical dissimilarity of the two materials.

The Effect of Moisture on the Emanating Power of Preparations containing Actinium.

After the comparisons recorded, the solution of Preparation II was evaporated to dryness on a crucible lid, ignited for an hour in an air-bath at 250° and an active deposit test carried out in the ordinary way, after the preparation had been exposed for some hours to the air of the laboratory. Under these conditions the amount obtained was the same as that given by the solution, only about a fourth of that originally given. The preparation was then put in a closed vessel containing water, and after some hours' exposure to the humid atmosphere, an active deposit test was made within the vessel in air saturated with moisture. Now the active deposit given was increased three times, and was very nearly equal to that originally given before the chemical treatment. Similarly it was found that the minute insoluble residue, in which no actinium could be detected dry, after exposure in the humid atmosphere, gave an active deposit nearly a third as great as that given by the preparation in the test last described. The whole series of tests is consistent with the view that the emanating power of the original preparation was near the maximum, and the actinium was that which corresponds with about 0·25 grm. of the original pitchblende. On further exposure to moisture the emanating power of the insoluble part diminished, and notable deliquescence was found to have occurred. The emanating power of the preparation from Joachimsthal pitchblende was increased 1·8 times by moisture, but further exposure also in this case caused a diminution. Evidently the problem of finding a quantitative radiometric method for the estimation of actinium, which shall be suited for these minute quantities,

and the long term of years over which the measurements must be conducted, will not prove an easy one to solve, but, until it is solved, it will not be possible to determine with absolute certainty the exact form of the growth-curve, and to settle the question whether the growth is linear with the time, and therefore direct.

Summary.

(1) In a full historical introduction, the data obtained in 1909 relative to the rays and products of uranium-X are discussed in so far as they throw light on the various possible modes of origin of actinium.

(2) The minute growth of actinium previously put on record in 1913 as having been observed in the old uranium-X preparations has been confirmed by their later history and is now established beyond doubt.

(3) Uranium-X_2 can be separated from uranium-X_1 by sublimation in a current of air charged with vapours of carbon tetrachloride at a temperature below visible red-heat.

(4) 470 grm. of a very pure Indian pitchblende were similarly treated, in the expectation of removing eka-tantalum, isotopic with uranium-X_2 and giving actinium in an α-ray change of long period.

(5) The preparations so obtained were initially free from actinium, but one of them has produced it continuously with the lapse of time.

(6) A direct comparison of the amount of actinium in this preparation after the lapse of 2·5 years with that in the original pitchblende showed that it was equal to that in about 0·25 grm.

(7) On the assumptions that eka-tantalum and actinium are both long-lived, that no intermediate members intervene between them, and that the preparation contained the whole of the parent of actinium in the original mineral, the period of average life of actinium is calculated to be 5000 years. Nothing can yet be said definitely as to the period of the parent.

(8) A second preparation separated from Joachimsthal pitchblende, the treatment of which commenced in 1903 and ended in 1914 with the carbon tetrachloride sublimation, has given a similar growth of actinium.

(9) The work was undertaken to test and confirms the view that the parent of actinium occupies the eka-tantalum place in the Periodic Table, and gives actinium in an α-ray change of long period, itself being formed as the product of uranium-Y, discovered by Antonoff, who suggested that it was the first member of the actinium series. But this mode of origin of actinium, though at present the most probable, has not yet been conclusively established to the exclusion of all the other possible modes of origin, discussed in the historical introduction.